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# Carbon and Phosphorus Cycling in Arabian Sea Sediments across the Oxygen Minimum Zone

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## Abstract

Several studies have focused on carbon, oxygen, and phosphorus dynamics across the modern oxygen minimum zone (OMZ) to constrain how signals of modern systems get "locked in" upon burial. In this study, a sequential phosphorus fractionation technique was applied to surficial and sub-surface sediments from stations at depths spanning the OMZ on the Pakistan margin of the Arabian Sea in order to test the oxygen-carbon-phosphorus connection in modern marine sediments. Some early diagenetic loss of phosphorus compared to organic carbon was observed, but a significant portion of the released phosphorus was retained by uptake on oxyhydroxides and by the formation of an authigenic phosphorus-bearing phase. This process is unaffected by station location relative to the OMZ, and results in an effective organic carbon-to-reactive-phosphorus sediment ratio that is close to the average observed for open-ocean sediments, regardless of bottom water oxygen content.

**Keywords:** Phosphorus; Carbon; Oxygen; Cycling; Arabian Sea; Fluxes

## Introduction

The importance of understanding the marine cycling of carbon (C) and phosphorus (P) cannot be overstated: C plays key roles in biological processes and climate modulation, and P is the key nutrient that limits cycling in the ocean on geologic timescales [1] and indeed may drive future ocean oxygenation due to human inputs of P to the ocean [2,3]. Several aspects of marine P cycling have been significantly clarified over the past several decades, including the importance of continental margin sinks in the P mass balance [4-10], the active diagenesis and transformation of P-bearing components in the water column and sediments [11-15], and the ubiquity of the authigenic mineral carbonate fluorapatite (CFA) as a long-term sink of P in the marine cycle [16-18]. In contrast to several of these "knowns," research into the interplay between C and P diagenesis and burial in low-oxygen environments has yielded a variety of apparently contradictory interpretations.

At the heart of this controversy is to what extent C and P cycling are decoupled during diagenesis. In particular, earlier scenarios called for the vast majority of reactive P sedimentation to the seafloor to be in the form of organically-bound P compounds. A variety of studies focusing on low-oxygen environments note somewhat higher-than-Redfield ratios in the organic matter fraction [19], but also find a significant role of iron in the burial and diagenetic cycle of P [20-23]. This dialog, and a satisfactory understanding of coupled C and P cycling in modern environments, can be informed by continued detailed studies focused on environments that receive similar sedimentary inputs but span a range of oxygen contents to clarify the role of oxygenation.

We focus here on a depth transect across several portions of the Arabian Sea continental margin (Figure 1) ;that spans the well-developed Oxygen Minimum Zone (OMZ) and has been the focus of a number of complementary studies on the modern and past nature of biogeochemical cycling. Our approach is to examine C and P geochemistry in surficial samples from a wide range of site water depths, and couple this array with four short cores selected across the OMZ and aimed at understanding diagenesis of these elements upon shallow burial. Our study is supplemented by several other examinations of P geochemistry in the region, including an analysis of the role that phosphogenesis (the authigenic formation of CFA) plays in the ultimate burial of P [7,22,24] and the interplay between paleoredox variations and the reflux of P back to the water column, perhaps fueling higher productivity in the Oman and Somalian coastal upwelling zones and indeed across the entire basin. This link between paleoredox and surface productivity has also been the focus of other regional-scale studies in the Mediterranean, where the redox-P-productivity process was a significant factor driving Milankovitch-scale ecosystem changes during the formation of Mediterranean sapropel-marl sequences during the latest Miocene [25,26].

## Materials and Methods

### Study area and samples

Twenty six surface sediment samples (0-2 cm) were analyzed from station transects spanning above and below the depths at which the mid-water (ca. 200-1000 m) OMZ impinges on the Pakistan continental margin of the northeastern Arabian Sea (Figure 1) [27]. These samples were from three different transects in contrasting areas, albeit with identical oxygen profiles, and there was one additional sample site on Murray Ridge. The samples were collected in September 1993. Given the sedimentation rate and pore water exchange rates; seasonal OMZ variations probably do not impact the bulk sample significantly given that these were sediment composite samples of 0-2 cm from box cores. The sediments recovered, from station depths of ca. 100 to 2900 m, ranged from coarse shelly sands on the shelf to fully laminated (varved) silty clays within the OMZ, to similarly fine but progressively more bioturbated sediments below [28]. Bottom topography on the

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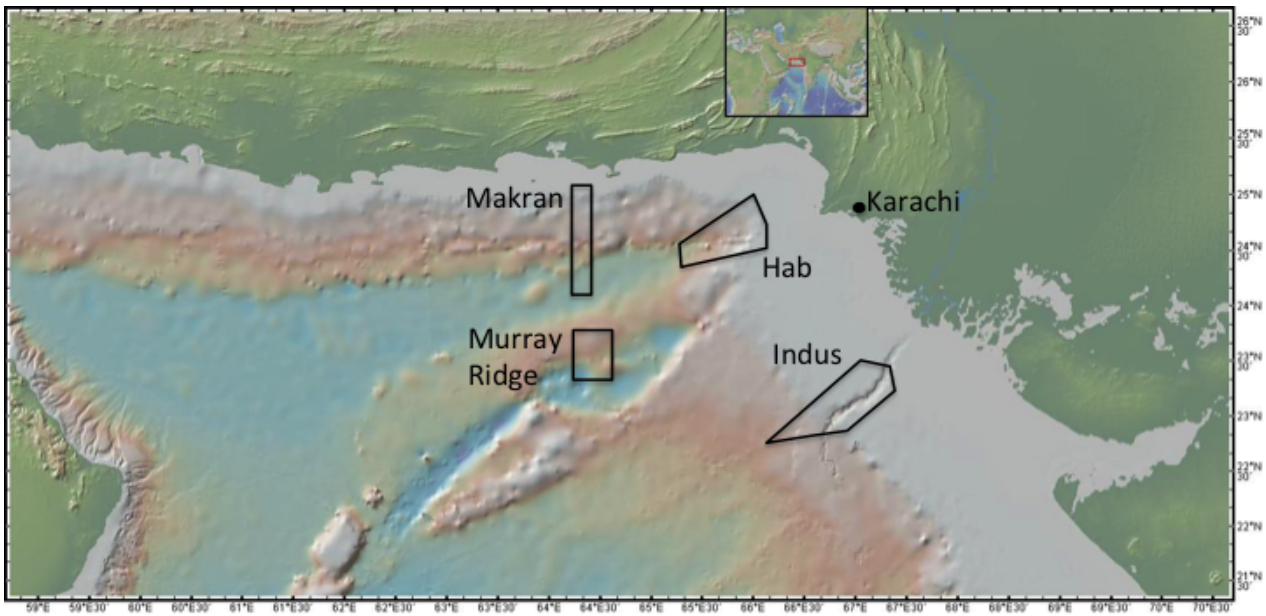


**Figure 1:** Site map showing wider study area (insert), bathymetry and primary station locations off the Indus margin of the NW Arabian Sea (Pakistan).

tectonically active Hab and especially the Makran transects was highly irregular and sediment records were frequently interrupted by local mudflow deposits. The Indus transect, by contrast, was topographically more uniform and gradual, and laminated sediments within the OMZ were regular and uninterrupted over full box-core lengths (up to 60 cm). The OMZ is here defined by the depths between which recovered sediments were lacking in burrows or other evidence of benthic macrofauna, and/or showed evidence of regular, annual laminations. However, bottom-water oxygen concentration ranges were also estimated at each coring site based on oxygen sensor casts at proximal offshore stations [27].

The surficial sediment samples provide an insight into net sediment/water geochemical characteristics across the OMZ. Benthic flux chambers and pore water profiles have revealed the active geochemistry and reactivity of sedimentary P, and are excellent for elucidating P cycling on seasonal, annual and decadal time scales [1,11,29,30], but the net removal of P (and C) from the reactive marine system on geologic timescales depends on the examination of longer (i.e., >1000 y) solid-phase records. To achieve this goal here, sediment depth profiles from four of the stations (136, 776, 1206, and 1506 m) on the Indus Margin transect (Figure 1), with maximum depths to 45 cm, were also chosen to bracket the range in bottom water oxygen, laminations, and sedimentation rates encountered along the margin.

## Analytical techniques

Excess $^{210}$Pb profiles [27] were obtained for the four sediment cores by standard beta-counting techniques [31,32]. The derived linear sedimentation rate for the laminated sediments at the site within the core of the OMZ (776 m) was ~0.6 mm/yr., which closely matched observed varve thickness. The site immediately below the OMZ (1206 m), yielded homogeneous sediments but no evidence of extensive bioturbation. The depth profile for this site yielded an identical excess $^{210}$Pb inventory and an identical (maximal) sediment accumulation rate (0.6 mm/y) to those observed at 776 m, in the core of the OMZ. Sites above and well below the OMZ (136 and 1506 m, respectively) showed homogeneous and extensively bioturbated sediments, with maximal estimated sedimentation rates of ca. ~1.5 mm/yr. It should be noted, however, that 14C-based sedimentation rates from other cores recently recovered from the Indus margin are lower than $^{210}$Pb -based rates at any site even with moderate bioturbation (Cowie, unpubl. data), and thus linear sedimentation rates at the three depths outside of the core of the OMZ should be considered maximal.

Geochemical analyses performed for this study included a sequential extraction for detailed P geochemistry and related reducible Fe determinations. Additional analyses of organic carbon ($C_{org}$), total nitrogen, bottom water oxygen, and bulk geochemistry were presented previously in Cowie et al. [27]. Inorganic carbon contents were determined by coulometry (Coulometrics, Inc.) while total carbon (organic C by difference) and total nitrogen were determined with a Carlo Erba 1500 CN analyzer (both methods as described by Cowie et al. [27]), with a standard error for all parameters ≤ 2.6%.

A sequential extraction procedure was used to isolate four operationally-defined P fractions: (1) reducible and easily desorbed P, (2) P associated with biogenic and/or authigenic phases, (3) organically-bound P ($P_{org}$), and (4) detrital P reflecting terrigenous input. This technique was modified from existing soil fractionation techniques and optimized for marine sediments [33]; these techniques have recently been used to explore P geochemistry in a number of settings [34-38]. By fractionating sedimentary P sinks, important details of P geochemical cycling during sediment diagenesis can be assessed.

The procedure outlined by Anderson and Delaney [19] after Ruttenberg [33] was used to separate and analyze the four P fractions. Approximately 0.2 g of each sample was weighed into a 15 mL polyethylene centrifuge tube. Samples with reagents were shaken on an orbital shaker for the prescribed amount of time, and then centrifuged for 10 minutes. All supernatants were decanted into acid-cleaned polyethylene bottles, and saved for analysis. A Shimadzu scanning UV-Visible Spectrophotometer was used for the determination of P concentrations for steps II-IV from the sequential P extraction using the molybdate blue technique for color development [39]. Dithionite-extractable P concentrations were

determined by ICP-AES because the CDB solution interferes with the standard color development. Randomly-chosen replicates were analyzed with an agreement within 6%.

The samples were processed and stored under normal oxygen concentrations. Because they were not stored and analyzed under anoxic conditions, any sulphide-bound Fe would oxidize relatively quickly, and would then be extracted in the CDB step of the P extraction. This could lead to Fe-oxides being extracted from within and below the OMZ, although within the OMZ they might be a product of post-sampling oxidation (see Supplementary Materials for a discussion of analytical uncertainties).

## Result and Discussions

Degradation of organic matter at these sites occurs via both oxic and suboxic pathways, and a rough correspondence exists between the maximum in surficial sedimentary organic C content and the minimum in bottom-water oxygen content, suggesting some control of dissolved oxygen on sedimentary organic matter contents on this margin [27]. Other redox indicators (e.g., $I/C_{org}$, Mn/Al), however, show that elevated accumulation of organic matter occurs even in more oxidized and homogenized sediments below the strict OMZ, indicating that the link between organic matter accumulation and $O_2$ availability is not straightforward [40].

### Relationship between organic phosphorus and organic carbon across the OMZ

A strong and positive linear correlation exists between $P_{org}$ and $C_{org}$ concentrations in the surficial sediments ($r^2$=0.79, n=25). The net $C_{org}$:$P_{org}$ ratio (molar) of this relationship is 318 (±86), closer to the mean sediment ratio of 430 [41] than the mean Redfield ratio of 106 (Figure 2); reflecting the ratio in fresh marine organic matter). Higher-than-Redfield $C_{org}$:$P_{org}$ values have been linked to the preferential regeneration of $P_{org}$ compared to $C_{org}$ during diagenesis [42]. As these particular samples are surficial, the preferential loss of $P_{org}$ must be occurring either in the water column or during residence in surficial sediments. We explore these issues later in a discussion of depth trends, but several recent studies have indicated that the transformation process of $P_{org}$ is rapid and can even begin significantly in the water column [15,43,44]. Overall, the mean $C_{org}$:$P_{org}$ ratios found here show a modest elevation within the OMZ compared to above and below that (Figure 3) The values above the OMZ nearer the shoreline are slightly higher than those below the OMZ on the continental slope and rise, perhaps due to the influence of terrestrial organic matter with higher $C_{org}$:$P_{org}$ ratios than marine organic matter [6].

### Depth profiles

The diagenesis of P with sediment depth has been shown to be a significant factor in its reactivity and eventual burial. Most of the reactive P delivered to the sediment-water interface in high productivity continental margin settings is associated with organic matter [34,45], with subsequent redistribution of P during organic matter degradation involving iron oxyhydroxides and authigenic mineralization as carbonate fluorapatite (CFA). This redistribution (so-called 'sink-switching'; Ruttenberg and Berner [16]) may greatly affect the sedimentary record of P cycling. An additional source of mineralized P delivery to the seafloor is in fish teeth, bone, and scale material, which globally comprises ~30% of total P accumulation [7], and aeolian/riverine CFA and diatom-bound P P [22]. In the anoxic Saanich Inlet, British Columbia, the $C_{org}$:$P_{org}$ ratio increased from about 160 in surficial sediments to above 800 at depth (60 m or 7,000 ybp; Filippelli [5]). Although a portion of this increase was due to preferential regeneration of P and reflux to the water column, most (~80%) was accommodated by the formation of disseminated CFA in interstitial spaces of the sediments [5]. To examine the effects of sink-switching with depth across an oxygen gradient (Saanich Inlet was nearly continuously anoxic for the last ~7,000 years), four additional sites were chosen along the Arabian Sea margin, spanning a range of bottom water oxygenation levels, water depths, and sedimentation rates.

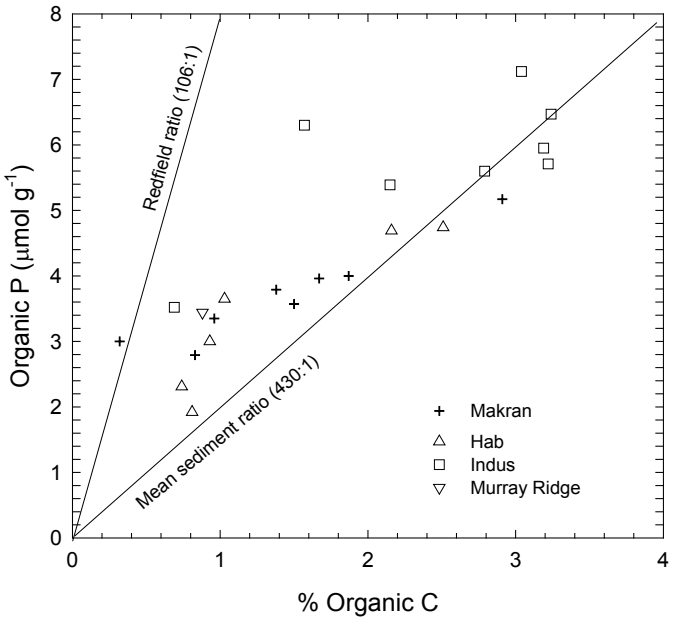


**Figure 2:** Organic carbon versus organic phosphorus in surface sediments of the Arabian Sea continental margin, along with the Redfield molar ratio values for fresh marine organic matter [54] and the mean sediment molar ratio [41].

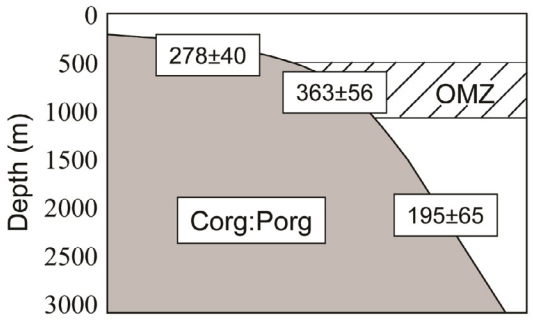


**Figure 3:** Molar organic carbon:organic phosphorus ratios with depth in surface sediments of the Arabian Sea continental margin. Mean $C_{org}$:$P_{org}$ ratios for surface sediments from above, within, and below the OMZ (Oxygen Minimum Zone) along the Arabian Sea continental margin. The mean $C_{org}$:$P_{org}$ of marine organic matter (Redfield ratio) is 106, that of oxic sediments is 200 [55], and that of anoxic sediments has been reported to range from at least 500 up to 4000 [42]. In the Arabian Sea setting, the net $C_{org}$:$P_{org}$ of surface sediments is only slightly elevated over average oxic sediments, even in laminated sediments from within the OMZ.

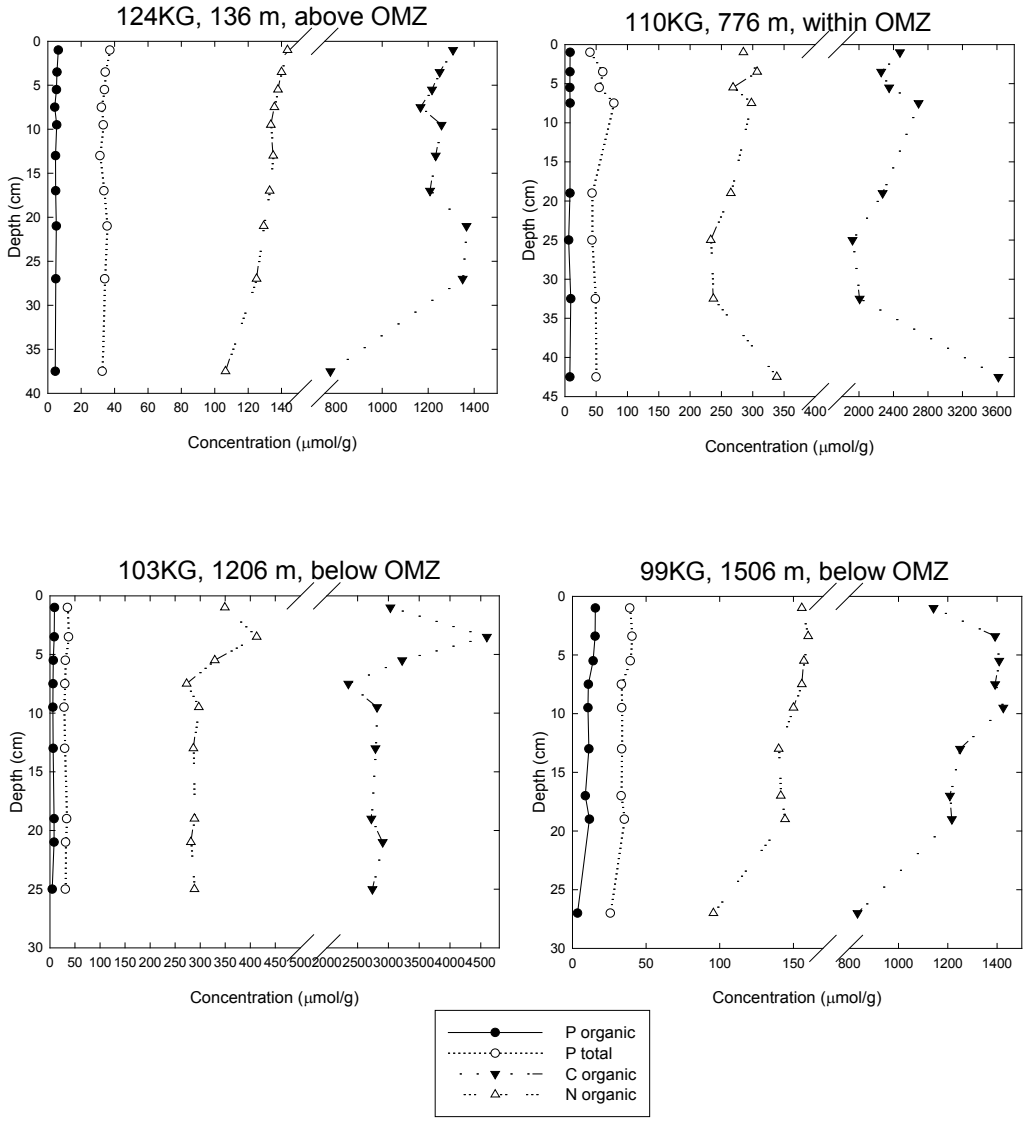


**Figure 4:** Downcore profiles of total phosphorus, and organic phosphorus, carbon and nitrogen, at four sites on the Arabian Sea continental margin from above, within, and below the Oxygen Minimum Zone.

In general, there is little evidence for diagenetic loss of organic matter downcore in sediments across the Pakistan margin (Figure 4). As illustrated by a series of cores from the Indus margin [27,46], there is generally little or no consistent downcore decrease in $C_{org}$ or N contents with sediment depth over the lengths of 40-60 cm sediment cores, and correspondingly little change in C/N ratios, with the exception of the relatively organic-matter-poor, bioturbated sediments well below the OMZ (where C and N contents, as well as C/N ratios, decrease downcore). Similar observations were made on the Hab and Makran margins [27]. This evidence for minor organic matter alteration was supported by general lack of downcore trends (for Indus margin cores) in pigment, lipid and amino acid content and composition [47,48]. This led to the conclusion, based also on indices of organic matter degradation state, that despite turnover of organic matter by benthic communities (fauna and microbes; [49-51], surficial sediment organic matter at all sites was comparatively degraded. Thus, organic matter content and composition was determined predominantly by decay within the overlying water column or across the sediment-water interface, prior to accumulation. This scenario is also consistent with the fact that, despite organic matter enrichment within the OMZ, only moderately reducing sediment redox conditions are observed, without progression to significant sulfate reduction within the upper 50-60 cm [52,53].

## Implications for P Burial in continental margin sediments

The rather predictable records of organic matter accumulation and burial over much of the margin are in contrast to the dynamic downcore P records (Tables 1 and 2). Although $C_{org}$:$P_{org}$ ratios were not observed to significantly change with the shallow depths examined here, the ingrowth of CFA was observed at all sites (Figure 5). Based on the increases in authigenic P concentrations (from 2.9 to 8.4 μg $P_{authigenic}$/kyr), the amount of authigenic CFA formed can be estimated to range from 0.02 to 0.1 wt% CFA (although as noted earlier, the $^{210}$Pb-modeled sedimentation rates for those bioturbated sites that lie outside of the OMZ are likely overestimates). This rate of CFA growth is high compared to high-productivity deep-sea settings (34), but is within the range of high-productivity continental margin settings [4,7]. These downcore records of CFA P might also be influenced to some degree by variation in the input of dust through time; dust in this region contains some CFA [22], which would presumably be delivered to the seafloor with little or no geochemical alteration before burial [2].

These samples record $C_{org}$:$P_{org}$ ratios above Redfield values of 106 [54], and above the reported mean oxic sediment value of about 200 [55]. A number of studies have used several techniques to constrain P cycling near the sediment-water interface, including benthic chamber experiments and pore water profiles. These studies have revealed a significant P reflux from the sediment to overlying waters in most, but not all, settings [11]. Even in the core of the OMZ, $C_{org}$:$P_{org}$ ratios only reach 434 (a finding similar to Anderson et al. [19]), well below values of 2000-4000 found in ancient marine black shales [56]. This finding is consistent with other work in the OMZ of the Eastern Arabian Sea, where Prakash Babu and Nagender Nath [56] found $C_{org}$/$P_{org}$ ratios of 322–447, and $C_{org}$/$P_{reactive}$ ratios close to Redfield (~106) in OMZ sediments from the SE Arabian Sea and slightly higher $C_{org}$/

| | Depth (m) | Area | [O2] +mol/L | Lamin/ Homogen | % org C | Oxide Fe mol/gm | Oxide P mol/gm | Organic P mol/gm | Auth/ Bio P | P Reactive mol/gm | Corg:Porg molar | C org:Preactive molar |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Arabiab Sea Site ID | | | | | | | | | | | | |
| 65 | 120 | Hab | 19 | H | 0.81 | 41.4 | 12.4 | 3.5 | 25.2 | 41 | 195 | 8.8 |
| 69 | 134 | Hab | 15 | H | 0.74 | 53.5 | 10.2 | 4.2 | 16.7 | 31 | 148 | 29.6 |
| 124 | 136 | | | H | | | 20.1 | 6.3 | 10.8 | 37.2 | 208 | 35.2 |
| 18 | 228 | Makran | 23 | H | 0.83 | 40.9 | 9.4 | 5 | 15.3 | 29.6 | 138 | 23.3 |
| 113 | 287 | Indus | 14 | L | 2.15 | 109.2 | 13.5 | 9.7 | 9.3 | 32.5 | 185 | 35.6 |
| 180 | 398 | Indus | 11 | L | 2.79 | 307 | 70.3 | 10.1 | 9.3 | 89.7 | 230 | 28.6 |
| 96 | 483 | Indus | 11 | H | 3.04 | 235.8 | 35.4 | 12.8 | 9 | 57.2 | 198 | 38.7 |
| 112 | 572 | Indus | 11 | L | 3.24 | 238.6 | 48.1 | 11.6 | 9.8 | 69.5 | 232 | 71.8 |
| 164 | 643 | Indus | 11 | L | 3.19 | 178.9 | 37.7 | 10.7 | 9.1 | 57.5 | 248 | 26.1 |
| 34 | 667 | Makran | 14 | L | 0.96 | 34.5 | 10 | 6 | 14.7 | 30.7 | 133 | 29.7 |
| 23 | 690 | Makran | 14 | L | 1.5 | 81.9 | 22.7 | 6.4 | 14.5 | 43.6 | 195 | 16.4 |
| 39 | 704 | Hab | 10 | L | 2.16 | 166.6 | 41.5 | 8.4 | 10.7 | 60.6 | 213 | 19.9 |
| 110 | 776 | | | L | | | 23.8 | 8.3 | 8 | 40.1 | 398 | 61.8 |
| 12 | 789 | Makran | 12 | L | 1.67 | 101.5 | 26.4 | 7.1 | 13.6 | 47.1 | 195 | 21.7 |
| 142 | 865 | Hab | 13 | L | 2.51 | 181.3 | 53.3 | 8.5 | 11.1 | 73 | 245 | 18.7 |
| 107 | 992 | Indus | 17 | L | 3.22 | 190.3 | 30.2 | 10.3 | 8.4 | 48.9 | 261 | 26.5 |
| 20 | 993 | Makran | 17 | L | 1.87 | 107.9 | 23.3 | 7.2 | 13.3 | 43.8 | 216 | 20.9 |
| 28 | 1017 | Makran | 19 | L | 2.91 | 77.9 | 12.9 | 9.3 | 11.6 | 33.8 | 261 | 44.3 |
| 24 | 1204 | Makran | 33 | H | 1.38 | 65.4 | 9.6 | 6.8 | 13.3 | 29.7 | 169 | 54.8 |
| 103 | 1206 | | | H | | | 18.1 | 9.1 | 9.3 | 34.8 | 333 | 87 |
| 99 | 1506 | | | H | | | 12.8 | 15.6 | 11.7 | 38.9 | 73 | 29.3 |
| 87 | 1782 | Murray | 83 | H | 0.88 | 114.1 | 9.4 | 6.2 | 12.1 | 27.6 | 119 | 38.8 |
| 79 | 1970 | Hab | 72 | H | 1.03 | 143.1 | 20.4 | 6.6 | 12.5 | 39.5 | 131 | 55.1 |
| 95 | 2111 | Indus | 91 | H | 0.69 | 80.4 | 8.7 | 6.3 | 12.5 | 27.5 | 91 | 28.7 |
| 1 | 2678 | Makran | 105 | H | 0.32 | 85.2 | 10.8 | 5.4 | 14.1 | 30.3 | 49 | 46.2 |
| 85 | 2881 | Hab | 106 | H | 0.93 | 121.5 | 22.3 | 5.4 | 13.7 | 41.4 | 143 | 25.9 |

**Table 1:** Geochemistry of surface sediments from the Arabian Sea Oxygen Minimum Zone transect. Sites 124, 110, 103, and 99 were cores from the Indus Margin and data presented here are from the top 0-2 cm of the cores.

| Depth (cm) | | Adsorbed P (mol/gm) | Oxide-bound(mol/gm) | Authigenic (mol/gm) | Organic P (mol/gm) | Reactive P (mol/gm) | Organic C (mol/gm) | Total N (mol/gm) | Corg: Porg (molar) | Corg: Preactive | Total N: Porg (molar) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 124 KG, 136 m, 1.5 mm/yr sed. rate, homogenous sediments | | | | | | | | | | | |
| 0-2 | 1 | 2.6 | 17.5 | 10.8 | 6.3 | 37.2 | 1308.3 | 143.6 | 207.7 | 35.2 | 22.8 |
| 3-4 | 3.5 | 1.9 | 16 | 11 | 5.5 | 34.4 | 1250 | 140 | 228.6 | 36.4 | 25.6 |
| 5-6 | 5.5 | 1.6 | 16.3 | 10.8 | 5.2 | 33.9 | 1216.7 | 137.9 | 233.6 | 35.9 | 26.5 |
| 7-8 | 7.5 | 1.6 | 15.7 | 10.6 | 4.2 | 32.1 | 1166.7 | 135.7 | 280.6 | 36.4 | 32.6 |
| 9-10 | 9.5 | 1.6 | 15.5 | 10.8 | 5.3 | 33.2 | 1258.3 | 133.6 | 236.8 | 37.9 | 25.1 |
| 12-14 | 13 | 1.6 | 15.4 | 9.6 | 4.6 | 31.2 | 1233.3 | 135 | 265.7 | 39.5 | 29.1 |
| 16-18 | 17 | 1.5 | 16 | 11.4 | 4.7 | 33.6 | 1208.3 | 132.9 | 257.1 | 36 | 28.3 |
| 20-22 | 21 | 1.4 | 16.7 | 12.3 | 5.1 | 35.5 | 1366.7 | 129.3 | 266.7 | 38.5 | 25.2 |
| 26-28 | 27 | 1.3 | 15.5 | 12.5 | 4.8 | 34 | 1350 | 125 | 283.2 | 39.6 | 26.2 |
| 35-40 | 37.5 | 1.2 | 15.2 | 11.7 | 4.5 | 32.6 | 775 | 106.4 | 172.5 | 23.8 | 23.7 |
| **110 KG, 776 m, 0.6 mm/yr sed. rate, laminated sediments** | | | | | | | | | | | |
| 0-2 | 1 | 4.2 | 19.6 | 8 | 8.3 | 40.1 | 2475 | 285 | 298.2 | 61.8 | 34.3 |
| 3-4 | 3.5 | 5.1 | 38.4 | 8.7 | 8.2 | 60.4 | 2258 | 307 | 275.4 | 37.4 | |
| 5-6 | 5.5 | 3.8 | 33.9 | 9.2 | 7.9 | 54.8 | 2350 | 268.6 | 296.3 | 42.9 | 33.9 |
| 7-8 | 7.5 | 3.1 | 57.3 | 9.5 | 8.3 | 78.2 | 2691.7 | 297.9 | 323.9 | 34.4 | 35.8 |
| 18-20 | 19 | 3.1 | 21.8 | 10.4 | 8.1 | 43.3 | 2275 | 265 | 282.4 | 52.5 | 32.9 |
| 24-26 | 25 | 2.9 | 23.1 | 11.2 | 6 | 43.2 | 1925 | 232.9 | 320.9 | 44.5 | 38.8 |
| 30-35 | 32.5 | 2.9 | 23.7 | 12.7 | 9.4 | 48.8 | 2008.3 | 237.1 | 212.7 | 41.2 | 25.1 |
| 40-45 | 42.5 | 2.7 | 25.8 | 13.1 | 8 | 49.6 | 3616.7 | 338.6 | 451.6 | 72.9 | 42.3 |
| **103 KG, 1206 m, 0.6 mm/yr sed. rate, homogenous sediments** | | | | | | | | | | | |
| 0-2 | 1 | 1.7 | 16.4 | 9.3 | 9.1 | 34.8 | 3033 | 349.3 | 332.6 | 87 | 38.3 |
| 3-4 | 3.5 | 1.7 | 19.2 | 9.3 | 8.6 | 37.1 | 4600 | 412.9 | 537.8 | 124.1 | 48.3 |
| 5-6 | 5.5 | 1.3 | 14.4 | 9.9 | 6.6 | 30.9 | 3225 | 329.3 | 488.6 | 104.5 | 49.9 |
| 7-8 | 7.5 | 1.4 | 13.7 | 9.7 | 6.3 | 29.7 | 2350 | 272.9 | 372.6 | 79.1 | 43.3 |
| 9-10 | 9.5 | 1.4 | 12 | 10.3 | 5.8 | 28.1 | 2816.7 | 297.1 | 484.8 | 100.2 | 51.1 |
| 12-14 | 13 | 1.5 | 13.1 | 9.7 | 6.5 | 29.3 | 2791.7 | 286.4 | 430.2 | 95.3 | 44.1 |
| 18-20 | 19 | 1.5 | 14.2 | 10.7 | 8.4 | 33.3 | 2725 | 288.6 | 323.9 | 81.7 | 34.3 |
| 20-22 | 21 | 1.3 | 13 | 9.9 | 8.4 | 31.3 | 2908.3 | 281.4 | 346.8 | 93 | 33.6 |
| 24-26 | 25 | 1.4 | 15.5 | 10.5 | 4.6 | 30.6 | 2741.7 | 288.6 | 591.6 | 89.6 | 62.3 |
| **99 KG, 1506 m, 1.2 mm/yr sed. rate, homogenous sediments** | | | | | | | | | | | |
| 0-2 | 1 | 1.1 | 11.7 | 11.7 | 15.6 | 38.9 | 1142 | 155.7 | 73.3 | 29.3 | 16.7 |
| 3-4 | 3.4 | 1 | 13.4 | 11.6 | 15.4 | 40.4 | 1391.7 | 160 | 90.5 | 34.5 | 24.7 |
| 5-6 | 5.5 | 1 | 13.2 | 11.9 | 14.1 | 39.2 | 1408.3 | 157.1 | 100.1 | 35.9 | 26.9 |
| 7-8 | 7.5 | 1 | 11.1 | 11.3 | 10.8 | 33.3 | 1391.7 | 155.7 | 128.4 | 41.8 | 39 |
| 9-10 | 9.5 | 1 | 11 | 11.8 | 10.8 | 33.4 | 1425 | 150 | 134.7 | 42.7 | 38.8 |
| 12-14 | 13 | 1.1 | 10.7 | 11.5 | 11.2 | 33.4 | 1250 | 140 | 111.6 | 37.4 | 32.6 |
| 16-18 | 17 | 1.1 | 11.6 | 12.7 | 8.7 | 33 | 1208.3 | 141.4 | 138.8 | 36.6 | 48.3 |
| 18-20 | 19 | 1.1 | 10.9 | 12.7 | 11.6 | 35.2 | 1216.7 | 144.3 | 105.2 | 34.6 | 32.3 |
| 26-28 | 27 | 1 | 8.8 | 13.4 | 3.5 | 25.7 | 833.3 | 95.7 | 239.1 | 32.4 | 27.5 |

**Table 2**: Downcore geochemistry at four sites across the Oxygen Minimum Zone in the Arabian Sea.

$P_{org}$ ratios (341–508), and lower-than Redfield $C_{org}/P_{reactive}$ ratios in OMZ sediments from the NE Arabian Sea. In both cases, they observed diagenetic transformation of P resulting in the accumulation of CFA at the expense of $P_{org}$. In contrast, at the higher terrigenous accumulation rate setting of the north Arabian Sea margin, Acharya et al. [57] found little evidence for sink-switching of P during shallow diagenesis, and indeed observed a net loss of reactive P back to the water column. Collectively, these studies indicate that both diagenetic loss and the potential for P "capture" are controlled by oxygenation as well as mineralogic template availability for CFA, particularly in the form of carbonates [34]. Variations in these factors with depth and along the Arabian Sea margin results in very different net burial characteristics and $C_{org}$:$P_{org}$ relationships, highlighting the hazards of using limited modern analogs to understand past processes.

Overall, the persistence of relatively low $C_{org}$:$P_{org}$ ratios in laminated and homogenous sediments and the strong correlation between these elements yields a potentially more complex picture of net C:P burial ratios in this setting. Sedimentation rate might play a role in modulating this ratio [4,58], as was found in the Eastern Arabian Sea as well [59]. Additionally, the mean annual state does not capture a more dynamic seasonal history in this and many other OMZs, where, for example, transient oxygen exposure might come from the shoaling of the upper OMZ boundary onto the shelf during the summer monsoon [46].

Burial rates of reactive P can be calculated from the sum of the P components, the sedimentation rate, and the dry bulk density, and here, sedimentation rate is again the prime controlling factor (although

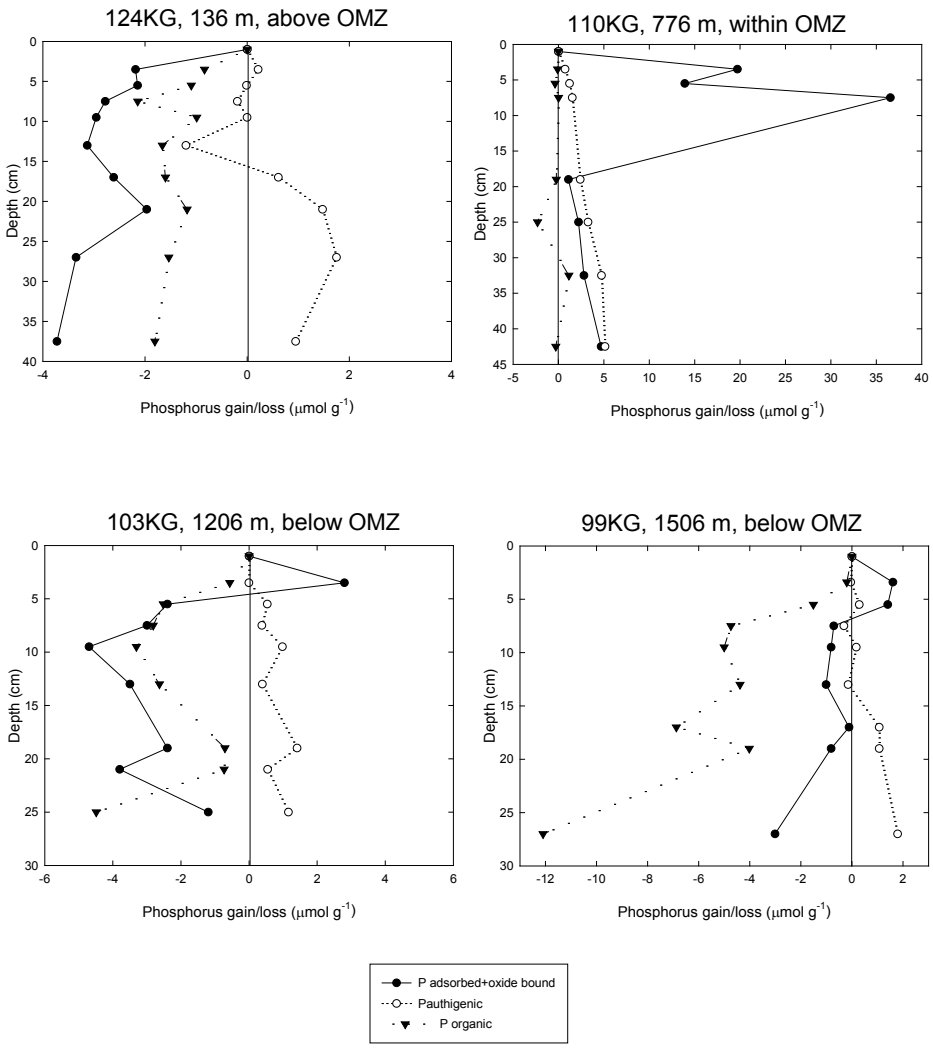


**Figure 5:** Downcore profiles phosphorus geochemistry at four sites on the Arabian Sea continental margin from above, within, and below the Oxygen Minimum Zone. Depth profiles reveal the ingrowth of an authigenic P-bearing phase (likely carbonate fluorapatite-CFA) at sites from above, within, and below the OMZ (Table 2). The solid-phase trends indicate extremely active authigenesis and P sequestration in the relatively insoluble CFA phase.

with the aforementioned caveats that the sedimentation rates modeled from $^{210}$Pb might be over-estimates in the areas below the OMZ). For example, P accumulation rates range from 624 μmol P/cm$^2$/kyr in the low sedimentation rate sites to 1,650 μmol P/cm$^2$/kyr in the high sedimentation rate sites, even though reactive P concentrations are about 25% higher in the former.

## Conclusion

In this study, a sequential P fractionation technique was applied to surficial and sub-surface sediments from stations at depths spanning the oxygen minimum zone (OMZ) on the Pakistan margin of the Arabian Sea in order to test the oxygen-C-P connection in modern marine sediments. Some early diagenetic loss of organic P compared to organic C generally occurs, but a significant portion of the released P was retained by uptake on oxyhydroxides and by the formation of an authigenic P-bearing phase. This process is unaffected by station location relative to the OMZ, surprising given broad assumptions about oxyhydroxide dissolution and related P release in low oxygen conditions. The relatively high retention rate of P results in an effective organic C to reactive P sediment ratio that is close to the average observed for open-ocean sediments, regardless of bottom-water oxygen content.

This finding of only a weak connection between oxygen and net P sequestration in modern marine sediments is supported by a number of other studies in low oxygen settings [5,7,11,22,23,60]. Lomnitz et al. [61] performed a detailed investigation of P cycling in the water column and surface sediments of the Peru margin OMZ and found little differences in C/P ratios under different redox regimes. Collectively, these results further confirm conclusions by others [61-63] that $C_{org}$:$P_{total}$ is a more robust indicator of preferential P release in response to bottom water oxygenation than is $C_{org}$:$P_{org}$. [64-70].

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